Inorg. Chem. **2003**, *42*, 7116–7122

Inorganic Chemistry
Article

Fluorination of $[Os_3(CO)_{12}]$ and $[Ir_4(CO)_{12}]$

In-Chul Hwang and Konrad Seppelt*

Institut für Chemie der Freien Universität, D-14195 Berlin, Germany

Received June 3, 2003

Fluorination of $[Os_3CO_{12}]$ in HF/SbF_5 affords $[Os(CO)_4(FSbF_5)_2]$. According to its crystal structure (orthorhombic, $Pna2_1$, $a = 1590.3(3)$, $b = 1036.6(1)$, $c = 878.2(2)$ pm, $Z = 4$), the two SbF_6 units occupy cis positions in the octahedral environment around the Os atom. Fluorination of $[Ir_4(CO)_{12}]$ in HF/SbF_5 produced three different compounds: (1) $[Ir_4(CO)_8(\mu\text{-}F)_2(Sb_2F_{11})_2]$ (tetragonal, $P\bar{4}n2$, $a = 1285.2(2)$, $c = 952.9(1)$ pm, $Z = 2$). Here, two of the six edges of the Ir_4 tetrahedron in $[Ir_4CO_{12}]$ are replaced by bridging fluorine atoms. (2) $[fac\text{-}Ir(CO)_3(FSbF_5)_2\text{-}HF]SbF_6\cdot HF$ (orthorhombic, $Pnma$, $a = 1250.6(1)$, $b = 1340.7(2)$, $c = 1092.6(2)$ ppm, $Z = 4$). The Ir_4 tetrahedron in $Ir_4(CO)_{12}$ is completely broken down, but the facial $Ir(CO)_3$ configuration is retained. (3) $[mer\text{-}Ir(CO)_3F(FSbF_5)_2]$ (triclinic, $P\bar{1}$, $a = 834.9(1)$, $b = 86\ 4.9(1)$, $c = 1060.0(1)$ pm, $\alpha = 69.173(4)°$, $\beta = 77.139(4)°$, $\gamma = 88.856(4)°$, $Z = 2$).

Introduction

Carbonyl cations have been known since 1961.[1] In the past decade, there has been enormous progress in the area, starting with $[Au(CO)_2]^+$ and $[Ag(CO)]^+$.[2,3] Three reviews on this subject have appeared recently.[4–6] The newest highlight is obviously the isolation of $Ir(CO)_6^{3+}(SbF_6^-)_3\cdot 4HF$.[7] This has been achieved by reductive carbonylation of IrF_6 in HF/SbF_5 with carbon monoxide. This method could also be used to obtain carbonyl cations with lower CO content. These would certainly be even more electrophilic. Indeed, $Ir(SO_3F)_3$ reacts with CO, forming $[mer\text{-}Ir(CO)_3(OSO_2F)_3]$,[8] which could be considered to contain the $Ir(CO)_3^{3+}$ cation, but the iridium−oxygen bond lengths of 203−206 pm point to a covalent nature. This is certainly a result of the basicity of the SO_3F^- anions. By making use of the superacidic system HF/SbF_5, as was done in the preparation of $[Ir(CO)_6]^{3+}$,[7] so that the less basic SbF_6^- and $Sb_2F_{11}^-$ anions are present, the electrophilic character of such carbonyl cations would become more obvious.

An alternative route to carbonyl cations of lower CO content could be the oxidation of metal carbonyls with low CO contents. As an early example, $[Ir_4(CO)_{12}]$ was fluorinated with XeF_2 in anhydrous HF. $[Ir(CO)_3F_3]$ as facial and meridional isomers was shown by NMR spectroscopy to exist in solution.[9,10] The structure of *fac*-$[Ir(CO)_3F_3]$ was elucidated by EXAFS because no suitable single crystals could be obtained. Ir−F bond distances were narrowed down to ca. 192 pm, and Ir−C distances, to ca. 203 pm.[10] $Os_3(CO)_{12}$ was fluorinated by XeF_2 in HF to predominantly *cis*-$[Os(CO)_4F_2]$ as well as $[Os(CO)_5F]$, $[Os_2(CO)_7F_4]$, and $[Os_2(CO)_8F_3]^+$. *cis*-$[Os(CO)_4F_2]$ was also identified in solution by means of NMR spectroscopy. [11] Recently, $[M_3(CO)_{12}]$ was fluorinated by fluorine gas in anhydrous HF to $[MF(\mu\text{-}F)(CO)_3]_4$ (M = Ru, Os).[12] These compounds, as well as others, can also be prepared by fluorination with XeF_2.[11,13]

Our approach was similar: we wanted to fluorinate $[Os_3(CO)_{12}]$ and $[Ir_4(CO)_{12}]$ in HF/SbF_5 solution, thus in the presence of the weakly coordinating anions SbF_6^- and $Sb_2F_{11}^-$, to arrive at crystalline materials, containing the weakly coordinating anions SbF_6^-or $Sb_2F_{11}^-$, that can be structurally characterized by X-ray diffraction.

---

* To whom all correspondence should be addressed. E-mail: seppelt@chemie.fu-berlin.de.

(1) Fischer, E. O.; Fichtel, K., Oefele, K. *Chem. Ber.* **1961**, *94*, 1200.
(2) Willner, H.; Aubke, F. *Inorg. Chem.* **1990**, *29*, 2195.
(3) Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 6277.
(4) Lupinetti, A. J.; Strauss, S. H., Frenking, G. *Prog. Inorg. Chem.* **2001**, *49*, 1.
(5) Willner, H.; Aubke, F. *Inorganic Chemistry Highlights*; Wiley-VCH: Weinheim, Germany, 2002; Vol. 1, p 195.
(6) Xu, Q. *Coord. Chem. Rev.* **2002**, *231*, 83.
(7) Ahsen, B. v.; Berkei, M.; Henkel, G.; Willner, H.; Aubke, F. *J. Am. Chem. Soc.* **2002**, *124*, 8371.
(8) Wang, C.; Lewis, A. R.; Batchelor, R. J.; Einstein, W. B.; Willner, H.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 1279.
(9) Brewer, S. A.; Holloway, J. H.; Hope, E. G.; Watson, P. G. *J. Chem. Soc., Chem. Commun.* **1992**, 1567.
(10) Brewer, A. A.; Brisdon, A. K.; Holloway, J. H.; Hope, E. G.; Peck, L. A.; Watson, P. G. *J. Chem. Soc., Dalton Trans.* **1995**, 2945.
(11) Brewer, S. A.; Holloway, J. H.; Hope, E. G. *J. Chem. Soc., Dalton Trans.* **1994**, 1067.
(12) Coleman, K. S.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Nassar, R. *J. Fluorine Chem.* **2001**, *112*, 185.
(13) Coleman, K. S.; Holloway, J. H.; Hope, E. G. *J. Chem. Soc., Dalton Trans.* **1997**, 1713.

10.1021/ic034611e CCC: $25.00

Experimental Section

Caution! *Handling anhydrous HF or compounds that produce HF upon hydrolysis requires eye and skin protection.*

Material and Apparatus. Synthetic work and sample handing were performed using Teflon-PFA ((poly)perfluoroether-tetrafluoroethylene) tubes that are sealed at one end and equipped at the other end with a metal valve and thus are connectable to a metal vacuum line. HF was dried by performing several trap-to-trap condensations and by discarding the less volatile fractions. SbF_5 (Merck) was purified similarly by discarding the highly volatile fractions. [$Os_3(CO)_{12}$] and [$Ir_4(CO)_{12}$] were commercially available (Sigma-Aldrich Co.) and used without further purification. XeF_2 was prepared from Xe and F_2 by irradiation according to the literature.[14]

Infrared spectra were recorded on a Bruker Vector 22 instrument, and Raman spectra, on a Bruker RFS 100 S instrument with Nd:YAG laser excitation ($\lambda = 1064$ nm). Raman samples were kept in the Teflon-PFA tubes, and the Raman scattering from the tubes was digitally subtracted. ^{13}C NMR spectra were recorded on a JEOL multinuclear instrument at 400 MHz. Spectra were recorded relative to TMS as an external standard. Elemental analyses were performed by Beller Co., Göttingen, Germany.

Single crystals were handled under cooling by approximately −120 °C cold nitrogen in a special device,[15] cut to an appropriate size, and mounted on a Bruker SMART CCD 1000 TU diffractometer using Mo Kα irradiation, a graphite monochromator, a scan width of 0.3° in ω, and a measuring time of 20 s per frame. After a semiempirical absorption corrections (SADABS) by equalizing symmetry-equivalent reflections, the SHELX programs were used for solution and refinement.[16] All atoms except hydrogen are refined anisotropically.

[$Os(CO)_4(FSbF_5)_2$]. In a glovebox filled with argon, H_2O, and O_2 of less than 1 ppm H_2O, 150 mg (0.496 mmol) of [$Os_3(CO)_{12}$] and 570 mg (2.63 mmol) of SbF_5 are weighed into a poly(perfluoro)ethene-vinyl ether (PFA) tube of 12-mm inner diameter. $Os_3(CO)_{12}$ dissolves in part. The PFA tube is connected to a stainless steel valve. On a metal vacuum line, 0.5 g (25 mmol) of HF is condensed at −196 °C. At room temperature, an orange solution is formed. A pressure of 2 bars of F_2 gas is maintained above the solution, which is kept at room temperature and shaken occasionally. The color changes from orange to yellow, after 1 min it turns green, and after 20 min it turns light blue. The procedure is stopped after several hours, when the solution is colorless. After pumping off all volatiles at room temperature, a colorless solid is formed (yield 200 mg). SbF_5 (1.8 g, 8.31 mol) and HF (1.75 g, 87.5 mmol) are condensed on the product, which dissolves completely at 60 °C. Slow cooling to room temperature afforded colorless crystals of [$Os(CO)_4(FSbF_5)_2$], mp 195−198 °C. IR spectrum (cm^{-1}, solid): 2226 (w), 2177 (m), 2153 (m), 2123 (m). Raman spectrum (cm^{-1}, solid): 2225(58), 2184(1), 2159(32), 2123(20), 707(3), 664(77), 651(20), 602(8), 580(2), 544(2), 481(26), 414(3), 383(3), 312(16), 295(17), 276(19), 218(10), 140(100). $^{13}C\{^{19}F\}$ NMR spectrum (d_6-acetone): 157.1 (s), 160.4 (s) ppm. Anal. ($C_4O_4F_{12}OsSb_2$, 773.7) C: calcd, 6.20; found, 5.99; F: calcd, 29.5; found, 29.5.

[$Ir_4(CO)_8(\mu\text{-}F)_2(Sb_2F_{11})_2$]. In a glovebox, 200 mg (0.181 mmol) of [$Ir_4(CO)_{12}$] and 185 mg (1.093 mmol) of XeF_2 are weighed into a PFA reaction tube of 12-mm inner diameter. The tube is connected to a stainless steel valve, and 300 mg (15 mmol) of HF are condensed on the mixture at −196 °C with the help of a metal vacuum line. Slow warming to −10 °C results in gas evolution and the formation of a yellow solution. All volatile material is pumped off at room temperature, leaving behind a yellow powder. In the glovebox again, 1.5 g (6.92 mmol) of SbF_5 is added, and 1.38 g (0.688 mol) of HF is condensed on the mixture. At 0 °C, a clear solution is formed. Cooling to −40 °C affords yellow, cube-shaped crystals, mp 85 °C. IR spectrum (cm^{-1}, solid): 2244 (vw), 2226 (w), 2184 (m), 2154 (m), 2170 (w), 2154 (w). Raman spectrum (cm^{-1}, solid): 2247(13), 2226(2), 2207(15), 2180(3), 653(100), 583(20), 491(20), 468(22), 288(52), 244(9), 222(8), 164(55), 118(74), 105(48). $^{13}C\{^{19}F\}$ NMR spectrum (d_6-acetone): 137.9 (s), 131.0 (s) ppm. Anal. ($C_8O_8F_{24}Ir_4Sb_4$, 1935.9) C: calcd, 4.96; found, 4.59; F: calcd, 23.6; found, 24.5.

[*fac*-$Ir(CO)_3(FSbF_5)_2(HF)$]SbF_6·HF. In a glovebox, 390 mg (0.353 mmol) of [$Ir_4(CO)_{12}$] and 360 mg (2.13 mol) of XeF_2 are weighed into a PFA reaction tube of 12-mm inner diameter. The tube is connected to a stainless steel valve. HF (300 mg, 15 mol) is condensed on this mixture at −196 °C at a metal vacuum line, gas evolution sets in a −70 °C, and the color of the solution changes from yellow to red-brown back to yellow. A black powder (350 mg) remains after pumping away all volatile materials: 3.2 g (14.7 mmol) of SbF_5 is added to this, and 570 mg (28.5 mol) of HF condenses on the mixture. Warming for 2 h at 50 °C affords a light-brown solution, and upon cooling, beginning at 40 °C, colorless cube-shaped crystals precipitate (mp 117 °C). IR spectrum (cm^{-1}, solid), Raman spectrum (cm^{-1}, solid): 2258(43), 2228(21), 2184(1), 707(22), 695(15), 681(58), 675(57); 667(100), 643(12), 611(16), 603(15), 576(7), 543(9), 453(19), 429(8), 384(14), 364(9), 296(31), 281(21), 268(23), 221(22), 204(20), 139(70). Anal. ($C_3O_3F_{20}IrSb_3$, 1021.5) C: calcd, 3.52; found, 3.54; F: calcd, 37.2; found, 36.0.

[*mer*-$Ir(CO)_3F(FSbF_5)_2$]. In a glovebox, 340 mg (0.31 mmol) of [$Ir_4(CO)_{12}$] and 1.42 mg (6.55 mol) of SbF_5 are weighed into a PFA reaction tube of 12-mm inner diameter. The tube is connected to a stainless steel valve. HF (620 mg, 31 mmol) condenses on the mixture by a metal vacuum line. At room temperature, a clear yellow solution is formed. F_2 (2 bars) is set for 6 h above the reaction mixture, which is kept at room temperature under occasional shaking. The yellow solution turns red-brown and then light yellow. The solution is cooled to −50 °C, and yellow, cube-shaped crystals are formed (mp 132 °C). IR spectrum (cm^{-1}, solid): 2262 (w), 2221 (m), 2201 (m), 2181 (w). Raman

---

(14) Holloway, J. H. *J. Chem. Soc., Chem. Commun.* **1962**, 22.
(15) Kottge, T.; Stalke, D. J. *Appl. Crystallogr.* **1993**, *26*, 615.
(16) Sheldrick, G. *SHELXS-93, Program for Crystal Structure Solution*; Universität Göttingen: Göttingen, Germany, 1986, 1993.

Table 1. Crystal Data for $[Os(CO)_4(FSbF_5)_2]$, $[Ir_4(CO)_8(\mu\text{-}F)_2\ (Sb_2F_{11})_2]$, $[fac\text{-}Ir(CO)_3(FSbF_5)_2HF]\ SbF_6{\cdot}HF$, and $[mer\text{-}Ir(CO)_3F(FSbF_5)_2]$

	$[Os(CO)_4(FSbF_5)_2]$	$[Ir_4(CO)_8(\mu\text{-}F)_2(Sb_2F_{11})_2]$	$[fac\text{-}Ir(CO)_3(FSbF_5)_2HF]SbF_6{\cdot}HF$	$[mer\text{-}Ir(CO)_3F(FSbF_5)_2]$
chemical formula	$C_4F_{12}O_4OsSb_2$	$C_8F_{24}Ir_4O_8Sb_4$	$C_3H_2F_{20}IrO_3Sb_2$	$C_3F_{13}IrO_3Sb_2$
fw	773.74	1935.88	1023.49	766.73
T, °C	−70	−100	−170	−170
space group	$Pna2_1$	$P\bar{4}n2$	$Pnma$	$P\bar{1}$
a, pm	1590.3(2)	1285.2(1)	1250.6(1)	834.9(1)
b, pm	1036.6(1)	1285.2(1)	1340.7(2)	864.9(1)
c, pm	78.2(2)	952.9(1)	1092.6(2)	1060.0(1)
α, deg	90	90	90	69.173(4)
β, deg	90	90	90	77.139(4)
γ, deg	90	90	90	88.856(4)
V, $10^6 pm^3$	1447.7	1573.9	1832.0	696.1
Z	4	2	4	2
μ, mm^{-1}	12.6	20.4	11.8	13.5
ρ_{calc}, g cm^{-3}	3.55	4.08	3.71	3.66
R, $[I > 4\sigma(I)]$	0.0193	0.0162	0.0316	0.0253
R, wR2(all data)	0.0229, 0.0396	0.0176, 0.0383	0.0328, 0.0680	0.0270, 0.0617

spectrum (cm^{-1}, solid): 2259(7), 2218(9), 2183(6), 687(49), 659(100), 601(15), 496(7), 466(7), 262(22), 244(18), 226(10), 126(21). $^{13}C\{^{19}F\}$ NMR spectrum (d_6-acetone): 143.6 (s), 140.3 (s) ppm. Anal. ($C_3O_3F_{13}IrSb_2$, 766.7) C: calcd, 4.70; found, 4.80; F: calcd, 32.6; found, 31.6.

Results and Discussion

The reaction of $[Os_3(CO)_{12}]$ with F_2 in HF/SbF_5 results in $[Os(CO)_4(FSbF_5)_2]$. This reaction (I) looks stoichiometrically simple,

$$^1/_3[Os_3(CO)_{12}] + F_2 + 2SbF_5 \rightarrow [cis\text{-}Os(CO)_4(FSbF_5)_2] \quad (I)$$

but according to the color change from orange to yellow to green to blue to colorless during the fluorination, it can be assumed that at least one intermediate, perhaps a blue one, is temporarily formed. Recently, another product, $[OsF(\mu\text{-}F)(CO)_3]_4$, was isolated under quite similar conditions except that the fluorination was done at −78 °C instead of at room temperature. It does not matter if the fluorination step is done in the presence of SbF_5 or if the latter is added later in the recrystallization—the outcome of the procedures is the same in this and all subsequent cases. Here, the final product, $[Os(CO)_4(FSbF_5)_2]$, is a colorless crystalline solid that is stable at room temperature. It is characterized by IR, Raman, and NMR spectroscopy and, most importantly, by the single-crystal structure determination (Tables 1 and 2 and Figure 1). There are no intermolecular contacts of any importance that influence the molecular shape. The osmium atom is octahedrally surrounded by four carbonyls and two fluorine atoms, the latter in cis fashion. These fluorine atoms belong to the two SbF_6 units. All angles at the osmium center are close to 90 and 180°. The bridging fluorine atoms have angles of 138.6(2) and 140.8(2)° and have strongly elongated Sb−F bonds (198.6(3) and 198.4(3) pm) if compared to the nonbridging fluorine atoms (184.4(3)−186.5(3) pm). As anticipated, the two Os−C bonds opposite the fluorine atoms are markedly shorter (190, 7(5), and 191.4(5) pm) than those of the mutually trans CO groups (199.2(5) and 203.6(4) pm). The osmium−fluorine distances are surprisingly short (208.8(3) and 212.1(3) pm). This is a direct indication of the electrophilicity of the hypothetical $(CO)_4Os^{2+}$ unit. The Os−C−O angles are nearly linear. The C−O bond lengths are all shorter than in free CO (112.82 pm). The extreme shortness of the (C(4)−O(4) bond (106.6(6) pm), however, is most likely due to the larger displacement parameters of the O(4) atom and thus is not real. The esd of this bond length should also be viewed with skepticism.

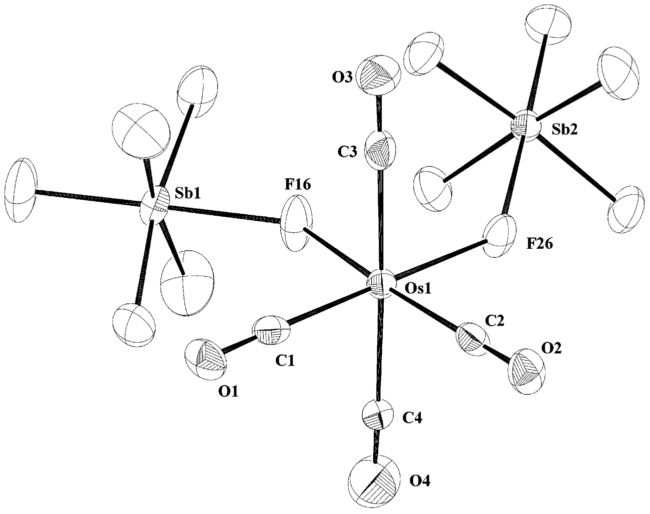

Figure 1. Crystal structure of $cis\text{-}[Os(CO)_4(FSbF_5)_2]$ with displacement ellipsoids at the 50% probability level.

Table 2. Important Bond Lengths (pm) and Angles (deg) for $cis\text{-}[Os(CO)_4(SbF_6)_2]$

Os−C(1)	190.7(5)	Sb(1)−F(11−15)	184.5(3)−185.5(5)
Os−C(2)	191.4(5)	Sb(1)−F(16)	198.4(3)
Os−C(3)	199.2(5)	Sb(2)−F(21−25)	184.4(3)−186.5(3)
Os−C(4)	203.6(4)	Sb(2)−F(26)	198.6(3)
Os−F(16)	208.8(3)		
Os−F(26)	212.1(3)		
C(1)−O(1)	111.8(5)		
C(2)−O(2)	111.7(5)		
C(3)−O(3)	111.2(6)		
C(4)−O(4)	106.6(6)		
C(1)−Os-C(2)	89.9(2)	Os−F(16)−Sb(1)	140.8(2)
C(3)−Os-C(4)	175.4(2)	Os−F(26)−Sb(2)	138.6(2)
F(16)−Os-F(26)	80.6(1)		
Os−(C(1)−O(1)	177.9(4)		
Os−C(2)−O(2)	179.4(4)		
Os−C(3)−O(3)	179.2(5)		
Os−C(4)−O(4)	177.6(5)		

The SbF_6^- groups act as monodentate ligands; two extreme descriptions of the binding situation would be zwitterionic species $Os(CO)_4^{2+}(FSbF_5^-)_2$ or an adduct between $Os(CO)_4F_2$ and two SbF_5 molecules. The compound closest to

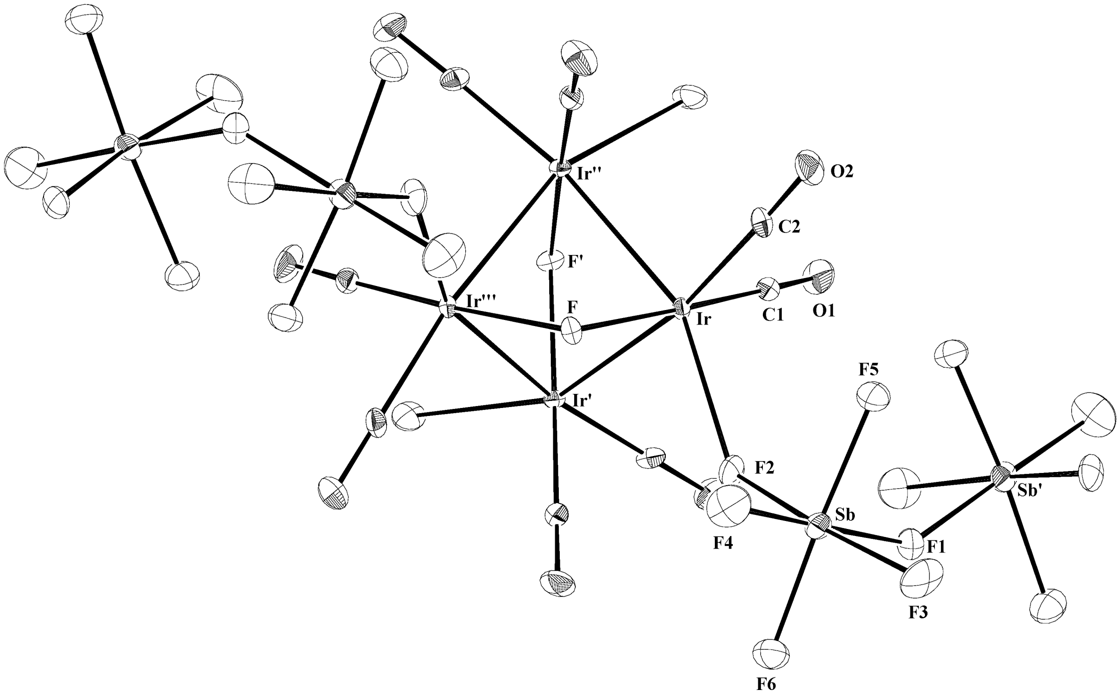

Figure 2. Crystal structure of [$Ir_4(CO)_8(\mu\text{-}F_2)(Sb_2F_{11})_2$] with displacement ellipsoids at the 50% probability level.

it seems to be [$\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$, except that here the molybdenum atom is seven coordinate because of the existence of three Mo−F−Sb bridges.[17] This is also the case in [$W(CO)_6FSbF_5$][Sb_2F_{11}].[18] Both of these compounds are made from $Mo(CO)_6$ or $W(CO)_6$ and SbF_5 in anhydrous HF.

The fluorination of $Ir_4(CO)_{12}$ gave more than one compound, and again, color changes during the fluorination are indicative of one or more intermediates that have not yet been isolated. The outcome of the fluorination, with F_2 or XeF_2, was dependent on the reaction time and the acidity of the HF/SbF_5 solution (i.e., concentration ratio HF/SbF_5). As anticipated, long fluorination times led to a complete breakdown of the Ir_4 cluster into mononuclear complexes, and short reaction times resulted in a fluorinated tetrameric Ir cluster, the latter of which needed a highly acidic solvent mixture for crystallization.

In the fluorinated tetrameric cluster [$Ir_4(CO)_8F_2$](Sb_2F_{11})$_2$, two of the six intermetallic bonds have been replaced by fluorine bridges. As shown in Figure 2, the $Sb_2F_{11}^-$ anions coordinate to the positions formerly occupied by CO ligands (one Ir−F(Sb) bond per Ir atom). The fluorine bridges exhibit quite short Ir−F distances of 206.5(2) pm, and the angle Ir−F−Ir is 98.4(1)°. The $Sb_2F_{11}^-$ anion is bent at the central fluorine atom (147.2(2)), as is usually observed. The Sb−F2 bond also has a contact to the Ir cluster, but the bond is only slightly elongated and the Ir···F2 contact is quite long (249.2(3) pm). A description of the entire molecular unit as [$Ir_4(CO)_8F_2$]$^{2+}$($Sb_2F_{11}^-$)$_2$ is justified. The iridium atoms are surrounded in a distorted octahedral manner, namely, by two other iridium atoms, the two fluorine atoms F1 and F12, and the two carbonyl groups. Each of the three pairs of Ir ligands have a cis orientation. The Ir−C(1) bond length opposite F1 is shorter than the Ir−C(2) bond length opposite the other iridium atom. The two C−O bond distances are of equal length within the esd's, and they are the longest ones among the four new compounds discussed in this paper.

[$OsF(\mu\text{-}F)CO)_3$]$_4$ and [$RuF(\mu\text{-}F)(CO)_3$]$_4$ can be regarded as the closest chemical relatives,[12,13] although they obviously do not have any intermetallic bonds. Detailed information on their structure is missing because of the lack of a crystal structure determination.

With respect to the fluorination, [$Ir_4(CO)_8F_2$] (Sb_2F_{11})$_2$ certainly represents one of the initial steps. The CO loss may occur during the final recrystallization from highly acidic HF/SbF_5 solutions.

A prolonged fluorination time for $Ir_4(CO)_{12}$ and a fairly low SbF_5 concentration in HF resulted in the isolation of [*fac*-$Ir(CO)_3(HF)(FSbF_5)_2$]SbF_6·HF (Figure 3 and Tables 1 and 4). The facial orientation of the three carbonyl ligands in [$Ir_4(CO)_{12}$] has been retained, and the Ir−Ir bonds of [$Ir_4(CO)_{12}$] are replaced by two SbF_6^- anions and one HF molecule. As in [$Os(CO)_4(FSbF_5)_2$], the two SbF_6^- anions function as ligands, but here the bridging fluorine atoms are closer to the Ir atom (203.1(5) pm) than to the Sb atom ((204.7(5) pm). This indicates the greater electrophilicity of the $Ir(CO)_3)^{3+}$ moiety relative to that of $Os(CO)_4^{2+}$. The sixth ligand is a HF molecule, so the molecular unit can be described as [*fac*-$Ir(CO)_3(FSbF_5)_2(HF)$]$^+SbF_6^-$·HF, with a nearly octahedral environment around the Ir atom. Counteranion SbF_6^- in the crystal is disordered over two close positions. This does not affect the cation, as shown in Figure 3 and Table 4.

The C−O bond lengths are remarkably short (109.8(11)

---

(17) Bröchler, R.; Freidank, D.; Bodenbinder, M.; Shan, I. H. T.; Willner, H.; Rettig, S. J.; Trotter, J.; Aubke, F. *Inorg. Chem.* **1999**, *38*, 3684.

(18) Bröchler, R.; Shan, I. H. T.; Bodenbinder, M.; Schmitz, V.; Rettig, S. J.; Trotter, J.; Willner, H.; Aubke, F. *Inorg. Chem.* **2000**, *39*, 2172.

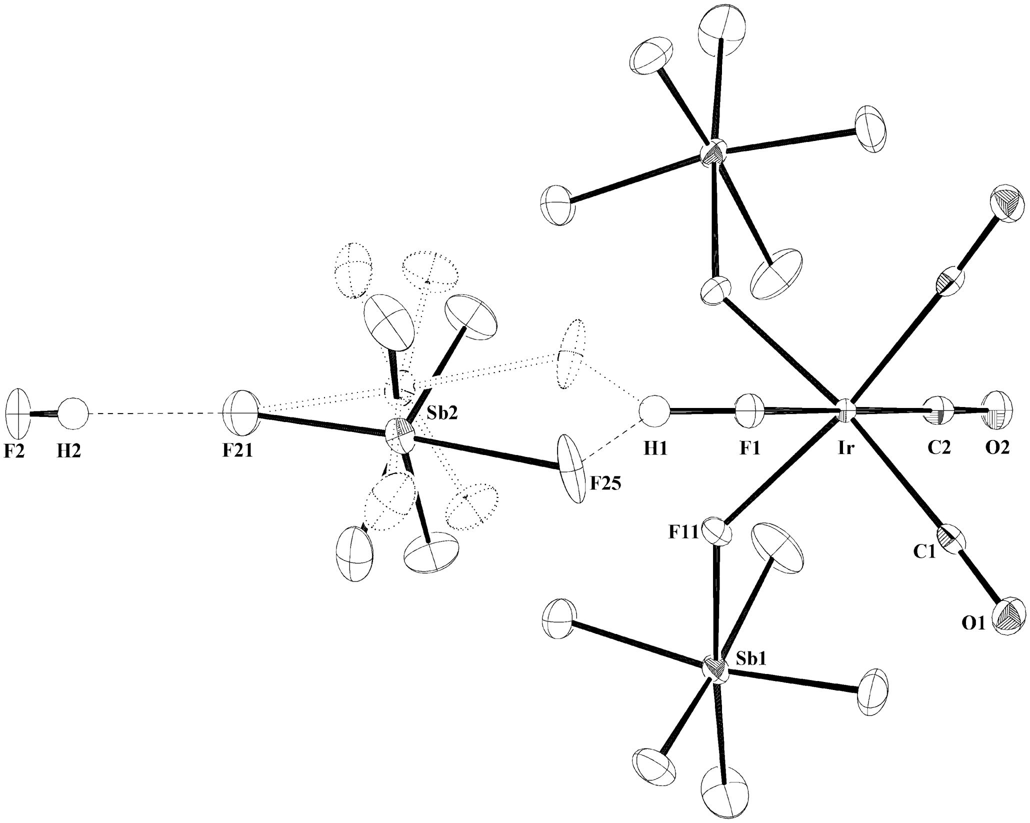

Figure 3. Crystal structure of [*fac*-$Ir(CO)_3(FSbF_5)_2HF]SbF_6\cdot HF$ with displacement ellipsoids at the 50% probability level. The disordered SbF_6^- unit is shown in the two orientations (dashed).

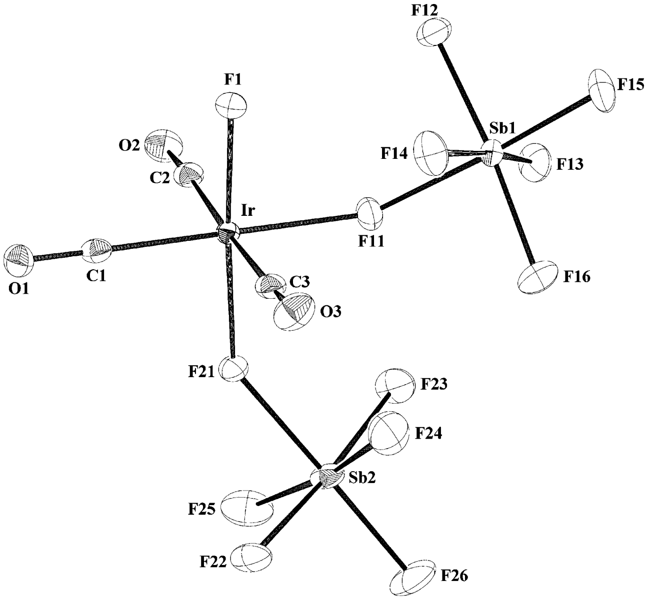

Figure 4. Crystal structure of [*mer*-$Ir(CO)_3F(FSbF_5)_2$] with displacement ellipsoids at the 50% probability level.

Table 3. Important Bond Lengths (pm) and Angles (deg) for $[Ir_4(CO)_8(\mu\text{-}F)_2(Sb_2F_{11})_2]$[a]

Ir−C(1)	183.3(4)	Sb−F1	203.0(1)
Ir−C(2)	190.6(5)	Sb−F2	188.6(3)
Ir−F	206.5(2)	Sb−F(3)	184.5(3)
Ir−F(2)	249.2(3)	Sb−F(4)	185.1(3)
Ir−Ir#1	262.71(2)	Sb−F(5)	186.4(3)
Ir−Ir#2	262.71(2)	Sb−F(6)	184.1(3)
Ir−Ir#3	312.62(3)		
C(1)−O(1)	112.7(5)		
C(2)−O(2)	113.1(6)		
C(1)−Ir−C(2)	89.8(2)	Sb−F(1)−Sb#4	147.2(2)
C(1)−Ir−F	173.9(1)	Sb−F(2)−Ir	142.5(2)
C(2)−Ir−F	95.1(1)	F(1)−Sb-F2	82.6(1)
Ir−C(1)−O(1)	177.3(4)	F(2−5)-Sb−F(3−6)	87.3(1)-96.9(2)
Ir−C(2)−O(2)	176.4(4)		
F−Ir−Ir#1	84.4(1)		
F−Ir−F(2)	76.8(1)		
Ir−F−Ir#3	98.4(1)		

[a] Symmetry transformations: #1: $1 + y, 1 - x, -z$; #2: $1 - y, x - 1, -z$; #3: $2 - x, -y, z$; #4: $0.5 + y, 0.5 - x, 0.5 - z$.

and 110.0(15) pm), but again, this finding can be in part a result of slightly enlarged displacement factors of some of the participating atoms.

Complexes containing the very weakly basic HF molecule as a ligand are still rare.[19] The donor properties of SbF_6^- and HF seem to be comparable if one considers the equal Ir−C distances opposite the SbF_6^- and HF ligands.

This *fac*-$Ir(CO)_3$ compound is unstable. It has not been possible to record a ^{13}C NMR spectrum without decomposition. In addition, the Raman spectrum, showing four carbonyl stretching bands, two of them quite weak, is also indicative of decomposition. The reason for this instability could be the presence of weakly bound HF. Its facile loss could result in the formation of other species.

In a solution of HF/SbF_5 with a higher concentration of SbF_5, $[Ir_4(Co)_{12}]$ is fluorinated to [*mer*-$Ir(CO)_3F(FSbF_5)_2$]. One could speculate that the higher acidity of the solvent catalyzes the facial−meridional isomerization via an ionic

---

(19) Transek, M.; Bencic, P.; Turicnik, A.; Tavear, B.; Zemva, B. *J. Fluorine Chem.* **2002**, *114*, 143.

Table 4. Important Bond Lengths (pm) and Angles (deg) for [*fac*-$Ir(CO)_3(SbF_6)_2HF$]SbF_6·HF[a]

Ir−C(1)	194.1(9)	Sb(1)−F(11)	204.7(5)
Ir−C(2)	194.5(12)	Sb(1)−F(12−16)	183.9(6)−186.8(6)
Ir−F(1)	200.5(8)	F(1)−H(1)	0.99(17)
Ir−F(11)	203.1(5)	Sb(2)−F(21−24)	183.8(9)−185.3(10)
C(1)−O(1)	110.4(7)		
C(2)−O(2)	110.6(10)		
C(1)−Ir−C(1)#1	93.0(5)	Ir(1)−F(11)−Sb(1)	133.5(3)
C(1)−Ir−C(2)	88.4(3)	Ir(1)−F(1)−H(1)	136.0(100)
C(2)−Ir−F(1)	179.8(4)	F(1)−Ir−F(11)	83.7(2)
C(1)−Ir−F#(11)#1	172.3(3)	F(11)−Ir−F(11)#1#11	80.0(3)
Ir−C(1)−O(1)	176.6(5)		
Ir−C(2)−O(2)	176.0(7)		

[a] Symmetry transformation: #1: *x*, 0.5 − *y*, *z*.

Table 5. Important Bond Lengths (pm) and Angles (deg) for [*mer*-$Ir(CO)_3F(SbF_6)_2$]

Ir−C(1)	189.7(5)	Sb(1)−F(11)	200.1(3)
Ir−C(2)	200.1(5)	Sb(1)−F(12−16)	184.7(3)−186.8(3)
Ir−C(3)	200.3(5)		
Ir−F(1)	191.6(3)	Sb(2)−F(21)	199.4(3)
Ir−F(11)	205.7(3)	Sb(2)−F(22−26)	184.7(4)−187.4(3)
Ir−F(21)	205.8(3)		
C(1)−O(1)	111.1(6)		
C(2)−O(2)	112.5(6)		
C(3)−O(3)	110.4(6)		
C(1)−Ir−F11	177.8(2)	Ir−F(11)−Sb(1)	139.9(2)
C(2)−Ir−C(3)	177.7(2)	Ir−F(21)−Sb(2)	140.2(2)
F(1)−Ir−F21	176.34(1)		
Ir−C(1)−O(1)	179.5(4)		
Ir−C(2)−O(2)	176.7(4)		
Ir−C(3)−O(3)	176.9(4)		

intermediate. The resulting compound is quite similar to [*cis*-$Os(CO)_4(FSbF_5)_2$] if one CO group is replaced by an F atom. The bridging fluorine atoms are, as in [$Os(CO)_4(FSbF_5)_2$], slightly closer to the Sb atom (200.1(3), 199.4(3) pm) than to the Ir atom (205.7(3), 205.8(3) pm), and the bridging angles are 139.9(2) and 140.2(2)°. The short Ir−F bond length of 191.6(3) pm to the terminal fluorine atom is noteworthy. This is only about 9 pm longer than in IrF_6.[20] The Ir−C distance trans to F11 is much shorter (191.6(3) pm) than the two mutually trans Ir−CO distances (205.7(3), 205.8(3) pm). This finding is similar to the previously described complexes. The C−O distances are short, (110.4(6)−112.5(6) pm), but there is again a possible distortion of the bond lengths due to the relatively large displacement factors.

Vibrational Spectra. Here we discuss only the CO stretching frequencies. Metal carbonyl cations are expected to have C−O distances shorter than in free CO (112.822 pm), and indeed this is found here in all of the species. But it is also known that a strong (essentially triple) bond shows only small bond-length variations dependent on subtle electronic effects, so other factors, as discussed previously, may override a significant shortening of the bonds. The carbonyl stretching frequencies, however, serve as a much better tool for the purpose of discussing the CO bond strength. In [$Os(CO)_4FSbF_5)_2$], four CO stretching modes are expected and found; they would have to be assigned to two pairs of antisymmetric and symmetric CO stretching modes. Even without a finite assignment, it can still be said that the mean value is well above the stretching frequency in free CO (2143 cm^{-1}).

The same is true for $Ir_4(CO)_8(\mu\text{-}F)_2(Sb_2F_{11})_2$. The number of CO stretching frequencies would depend on the amount of vibrational coupling between the $Ir(CO)_2$ groups. The observation of four IR and six Raman C−O stretching modes indicates that the $Ir(CO)_2$ groups cannot be treated independently. Nevertheless, all frequencies are higher than in free CO.

In [*fac*-$Ir(CO)_3(FSbF_5)_2HF$]·SbF_6·HF and [*mer*-$Ir(CO)_3F(FSbF_5)_2$], all CO stretching frequencies are also well above the 2143-cm^{-1} value of free CO. This is a common phenomenon for almost all known metal carbonyl cations,[4−6] and it is usually explained by the weakness or absence of π back-donation.[4,5] As expected, the vibrational spectra of [*mer*-Ir(CO) F($FSbF_5)_2$] and [*mer*-$Ir(CO)_3(OSO_2F)_3$] are quite similar in the CO stretching region.[8]

Although the observed CO stretching frequencies are high, they are not the highest that have been observed for metal carbonyl cations. Possibly the highest frequencies are observed in $Ir(CO)_6^{3+}$,[7] $Pt(CO)_4^{2+}$,[21] and $Hg(CO)_2^{2+}$.[22,23]

^{13}C NMR Spectra. The ^{13}C NMR spectra can serve as qualitative indicators of the structure of these compounds in solution: two resonances of equal intensity were observed for [*cis*-$Os(CO)_4(FSbF_5)_2$], as expected for the cis configuration. Similarly, two lines of equal intensity were observed for [$Ir_4(CO)_8F_2$]($Sb_2F_{11})_2$ as a consequence of the nonequivalence of the two carbonyl groups on each Ir atom. Because of decomposition in solution, no reliable ^{13}C NMR spectrum has been obtained for [*fac*-$Ir(CO)_3(F{-}SbF_5)_2$](HF)·SbF_6·HF. [*mer*-$Ir(CO)_3F(FSbF_5)_2$] also exhibits two resonances, one of them (143.6 ppm) with a higher intensity than the one at 140.3 ppm.

There is no simple correlation between ^{13}C NMR data and ν_{CO}. Qualitatively, it can be stated that the higher ν_{CO}, the lower δ ^{13}C will be,[4] so triply charged $Ir(CO)_6^{3+}$ has the lowest chemical shift of 121 ppm.[7] Tentatively, we could therefore assign the higher-field resonance to those CO groups that are opposite to F atoms. This would be consistent with the relative intensities of the resonances in [*mer*-$Ir(CO)_3F(FSbF_5)_2$].

---

(20) Kimura, M.; Schomaker, V.; Smith, D. W. *J. Chem. Phys.* **1968**, *48*, 4001.

(21) Willner, H.; Bodenbinder, M.; Bröchler, R.; Hwang, G.; Rettig, S. J.; Trotter, J.; Ahsen, B. v.; Westphal, U.; Jonas, V.; Thiel, W.; Aubke, F. *J. Am. Chem. Soc.* **2001**, *123*, 588.

(22) Willner, H.; Bodenbinder, M.; Wang, C.; Aubke, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1189.

(23) Bodenbinder, M.; Balzer-Jöllenbeck, G.; Willner, H.; Batchelor, R. J.; Einstein, F. W. B.; Wang, C.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 82.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Penguin Foundation.

Supporting Information Available: Listings of the collection of data and refinement, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and drawings of the molecular unit. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034611E